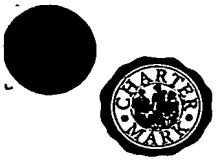

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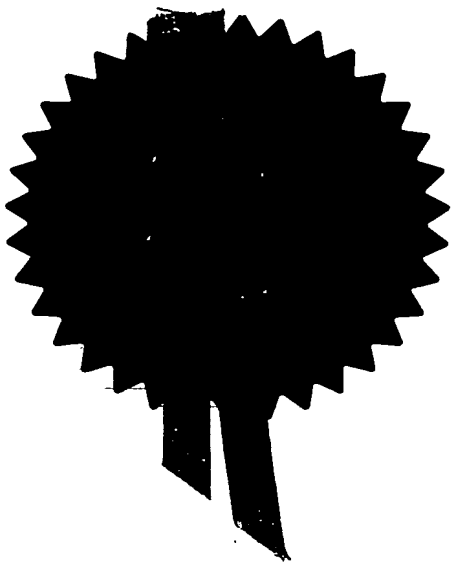

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26SEP03 E839766-1 D02852
F01/7700 0.00-0322483.9

1.	Your reference	AJF/P64314/000
2.	Patent application number *(The Patent Office will fill in this part)*	0322483.9
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	THERMO FINNIGAN LLC 355 RIVER OAKS PARKWAY SAN JOSE CALIFORNIA 95134-1991 UNITED STATES OF AMERICA
	Patents ADP number *(if you know it)*	8125817001
	If the applicant is a corporate body, give the country/state of its incorporation	DELAWARE, UNITED STATESOF AMERICA
4.	Title of the invention	MEASURING CELL FOR ION CYCLOTRON RESONANCE SPECTROMETER
5.	Name of your agent *(if you have one)*	BOULT WADE TENNANT
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	VERULAM GARDENS 70 GRAY'S INN ROAD LONDON WC1X 8BT
	Patents ADP number *(if you know it)*	42001

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Country	Priority application number (if you know it)	Date of filing *(day/month/year)*

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Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? **YES**

(Answer 'Yes' if:
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Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(Please specify)*	

11 I/We request the grant of a patent on the basis of this application.

Signature Date

25 September 2003

12. Name and daytime telephone number of person to contact in the United Kingdom **Dr. Alex Frost**
020 7430 7500

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MEASURING CELL FOR ION CYCLOTRON RESONANCE SPECTROMETER

This invention relates to a measuring cell for an Ion Cyclotron Resonance (ICR) spectrometer.

Fourier Transform Ion Cyclotron Resonance is a technique for high resolution mass spectrometry which employs a cyclotron principle.

One such FT-ICR spectrometer is shown in our co-pending Application No. GB 0305420.2 which is incorporated herein by reference in its entirety. As is described in that application, ions generated in an ion source (usually at atmospheric pressure) are transmitted through a system of ion optics employing differential pumping and into an ion trap. Ions are ejected from the trap, through various ion guides and into a measurement cell. In that cell, the field lines of a homogeneous magnetic field (generated by an external superconducting magnet, for example), extend along the cell in parallel with the cell's longitudinal axis. By applying an r.f. field, perpendicular to the magnetic field, the ions can be excited so as to produce cyclotron resonance. Charged particles in the cell then orbit as coherent bunches along the same radial paths but at different frequencies. The frequency of the circular motion (the cyclotron frequency) is proportional to the ion mass. A set of detector electrodes are provided and an image current is induced in these by the coherent orbiting ions. The amplitude and frequency of the detected signal are indicative of the quantity and mass of the ions. A mass spectrum is obtainable by carrying out a Fourier

Transform of the 'transient', i.e. the signal produced at the detector's electrodes.

Figure 1a shows, highly schematically, the arrangement of electrodes in a prior art cell. In particular, a section through a cell 10 is shown, along with its longitudinal axis z. An orthogonal section through the cell 10 is also shown in Figures 1d and 1e which show, respectively, the electrode arrangements in a cylindrical and in a square rectangular configuration respectively.

In Figure 1a, the cell 10 comprises a central electrode 20 and outer electrodes 30, 40 surrounding that. An r.f. voltage is applied to each of the electrodes so as to produce an excitation field, and a d.c. voltage is applied to the outer electrodes 30, 40 so as to provide a trapping field.

The trapping field created by the prior art arrangement of Figure 1a is shown in Figure 1b.

The longitudinal ("z") axis of Figure 1b is intended to be generally to the same scale as that of Figure 1a, so that the magnitude of the trapping field U in the z-direction of Figure 1b corresponds with the position along the z axis of the electrodes in Figure 1a. Figure 1b also shows the approximate range of the homogeneous field region of the applied magnetic field.

Figure 1c shows a schematic representation of equipotentials of the excitation field in the cell 10 of Figure 1a. It will be seen that the excitation field equipotentials are generally parallel to the z axis in the centre of the cell and close to the 'z' axis, so that there is no excitation electric field component in the z

direction, but curve significantly so that there is a non-zero excitation electric field component in the z-direction (see Figure 1g). Optimal excitation for FTMS requires an homogeneous electrical excitation field. R.f. electric field components in the radial direction of the cell cause the ions to gain energy in that (desired) radial direction. Any finite electrical excitation field component in the direction of the cell's longitudinal axis 'z' causes an acceleration in that axial direction. Longitudinal acceleration of ions is undesirable because the potential barrier in that direction is typically only of order 1 eV (higher trapping potentials causing unwanted field distortion) and so ions may easily escape from the cell and thus be lost.

One theoretical possibility to remove the axial r.f. field components towards the edges of the cell would be to make the electrodes of infinite length. The problem with this is that, as the electrodes become longer in the z-direction, so the ions reside in a volume that extends outside of the homogeneous zone of the magnetic field. This in turn causes a reduction in the resolving power of the spectrometer.

An alternative approach to the production of an excitation electric field with parallel field lines is described in US-A-5,019,706. Here, additional electric r.f. signals are applied to one or more of the trapping electrodes on both sides of the measuring cell. This causes the inhomogeneities in the field lines at the cell extremities (as a result of its finite length in the axial direction) to be balanced out by heterodyning with the additional r.f. field components which are introduced

by the trapping electrodes, so that the ions in the trap experience an r.f. field more like that which would be produced by a cell of infinite axial length. Lines of equipotential in the cell of US-A-5,019,706 are shown for the purposes of illustration only, in Figure 1f.

Nevertheless, the arrangement of US-A-5,019,706 suffers from the disadvantage that electrodes have to share the static trapping potential and the RF excitation potentials, which may increase the cost of the driving electronics and/or the amount of noise. Furthermore, the potential well which traps ions in the cell extends as far as the region of excitation field curvature in this arrangement so that trapped ions still experience an inhomogeneous excitation field, as may be seen from Figure 1f.

Against this background, there is provided, in a first aspect, a measurement cell for an FTMS spectrometer, comprising: a plurality of excitation electrodes arranged symmetrically about a longitudinal axis which extends in a direction generally parallel to the field direction of an applied homogeneous magnetic field; and a plurality of trapping electrodes, also arranged symmetrically about the said longitudinal axis; wherein at least some of the excitation electrodes are arranged axially outwardly of the trapping electrodes.

Placing at least some of the excitation electrodes axially outwardly of the trapping electrodes causes the non-linear region of the excitation field to be "pulled" axially outwards relative to the prior art arrangements so that the field lines are more linear in the region axially between the trapping electrodes in which the ions

are confined and where, in preference, the magnetic field is homogeneous.

In accordance with a further aspect of the present invention, there is provided a method of trapping and exciting ions in a measurement cell of an FTMS spectrometer, the method comprising: (a) applying a magnetic field to the measurement cell so as to produce a region of homogeneous magnetic field, having a magnetic field direction, within the cell; (b) applying a d.c. trapping potential to a plurality of trapping electrodes which are arranged symmetrically about a longitudinal axis which extends in a direction generally parallel to that magnetic field direction, so as to trap ions in the cell, in that axial direction; and (c) applying an r.f. excitation potential to a plurality of excitation electrodes which are arranged symmetrically about that longitudinal axis, so as to resonantly excite the ions in the cell, at least some of the excitation electrodes being arranged axially outwardly of the trapping electrodes; wherein the ions are trapped within the region of homogeneous magnetic field and wherein the ions are further trapped within a homogeneous region of an excitation electric field generated by the application of the r.f. excitation potential to the said excitation electrodes.

Further preferred features are set out in the dependent claims which are appended hereto.

The invention may be put into practice in a number of ways and some preferred embodiments will now be described by way of example only and with reference to the accompanying drawings, in which:

Figure 1a shows a schematic longitudinal section through a prior art FTMS measurement cell;

Figure 1b shows, to the same scale as Figure 1a, the d.c. trapping potential U along the longitudinal axis z of the cell of Figure 1a;

Figure 1c shows, again to the same scale as Figure 1a, lines of r.f. excitation equipotential τ along the longitudinal axis z of the cell of Figure 1a;

Figures 1d and 1e show views along the line AA of Figure 1a, for circular and square section cells respectively;

Figure 1f shows lines of r.f. excitation potential τ along the longitudinal axis of the measurement cell of US-A-5,019,706 which also forms a part of the state of the art;

Figure 1g shows the electrical field components of an arbitrary point on an r.f. excitation field equipotential of the cell of Figure 1a, towards the edges of that cell, along with an indication of the radial and axial components of force thereby applied to an ion at that point;

Figure 2a shows a schematic longitudinal section through an FTMS measurement cell in accordance with a first embodiment of the present invention;

Figure 2b shows, to the same scale as Figure 2a, the d.c. trapping potential U along the longitudinal axis z of the cell of Figure 2a;

Figure 2c shows, also to the same scale as Figure 2a, lines of equipotential for the r.f. excitation field τ along the longitudinal axis z of the cell of Figure 2a;

Figure 3a shows a schematic longitudinal section through an FTMS measurement cell in accordance with a second embodiment of the present invention;

Figure 3b shows, to the same scale as Figure 3a, lines of equipotential for the r.f. excitation field τ along the longitudinal axis of the measurement cell of Figure 3a; and

Figure 4 shows a schematic longitudinal section through an FTMS measurement cell in accordance with a third embodiment of the present invention.

Turning first to Figure 2a, a schematic longitudinal section through an FTMS measurement cell 100 in accordance with a first embodiment of the present invention is shown. The cell 100 is rotationally symmetrical about a longitudinal axis z and may, for example, be cylindrical or oblong in shape, as will be explained further below.

The cell 100 comprises a first pair of central excitation electrodes 110 which are located about an axially central point of the cell 100. Axially outward of this central pair of excitation electrodes 110, on either side thereof, are two pairs of trapping electrodes 120, 130. The trapping electrodes of Figure 2a have the same, or similar, diameter, to the first pair of excitation electrodes 110.

Axially outwardly of the pairs of trapping electrodes 120, 130 are second and third pairs of outer excitation electrodes 140, 150 respectively. Again, the diameter of these outer excitation electrode pairs is the same or similar to that of the trapping and central excitation electrode pairs. Thus, the outer electrode

pair 140 and the central electrode pair 110 'sandwich' the trapping electrode pair 120 between them, and the outer electrode pair 150 and central electrode pair 110 'sandwich' the trapping electrode pair 130 between them.

An r.f. voltage supply 160 is connected, in the embodiment of Figure 2a, to each of the excitation electrode pairs 110, 140, 150. Although a single r.f. voltage supply (of a given voltage) may be attached to ach of the excitation electrode pairs, different voltages and/or frequencies may instead be applied to each by virtue of voltage and/or frequency divider(s) respectively, or by using separate r.f. voltage supplies.

A d.c. voltage 170 is applied to the trapping electrodes 120, 130. Again, the same or different d.c. voltages may be applied to the two pairs of trapping electrodes 120, 130.

Figure 2b shows a schematic plot of the trapping field, U, as a function of axial position z. It will be seen that, in comparison with the prior art arrangement of Figure 1b, the trapping field has two clearly defined peaks 180 which coincide with the axial positions of the trapping electrodes 120, 130. The peaks then tail off sharply as the position z moves further away from the centre of the cell 100.

Figure 2c shows a schematic of the lines of equipotential of the excitation field generated in the cell 100 of Figure 2. It will be noted that the field lines are relatively flat and parallel with the z axis, across the bulk of the region of confinement of the ions which is between the two peaks 180 of the trapping potential U (Figure 2b). There is a small perturbation

190 in the excitation field in the region of the trapping electrodes, as is seen in Figure 2c, but this has not been found to affect the overall trapping and excitation unduly.

The arrangement of Figure 2a accordingly "pulls" the non-linear region of the excitation field outwards relative to the arrangement of Figure 1a so that the excitation electric field is essentially homogeneous in the trapping region. It will also be noted that the axial barriers formed by the peaks 180 in the trapping field coincide with the homogeneous area of the magnetic field (cf US-A-5,019,706, described above, where the (physical) axial barriers for trapped ions are in that case outside the homogeneous area of the magnetic field). Thus, high resolution FTMS measurements can be made (because a large proportion of trapped ions experience homogeneous magnetic and excitation fields) whilst the number of ions lost after injection into the cell 100 is minimized.

Although not shown in the Figures, it will be understood that the cell 100 of Figure 2 also includes detecting electrodes which may (as in the arrangements of Figure 1d or 1e) be radially interspersed with the trapping and excitation electrodes. It is advantageous to have the detecting electrodes and the trapping/excitation electrodes radially equally spaced from the axis z so as to retain symmetry.

Figure 3a shows an alternative arrangement of a measurement cell 100' to that of Figure 2a. Features common to these two Figures are nevertheless labelled with like reference numerals. In the cell 100' of Figure 3a, instead of connecting the r.f. voltage supply 160

only to the excitation electrodes 110, 140, 150, it is also connected, along with the d.c. voltage 170 to the trapping electrodes 120, 130. The logical layout of electrode potentials is shown in the upper part of Figure 3a. The physical layout, indicating one way of wiring the electrodes is shown in the lower part of that Figure. It will be seen that the r.f. and d.c. voltage supplies 160, 170 are decoupled from one another by employing a capacitance 200 between the r.f. and d.c. supplies to the trapping electrodes 120, 140, so that d.c. is not also supplied via the r.f. electrical leads to the excitation electrodes 110, 140, 150. Applying a combined d.c. and r.f. field in this way reduces the presence of the perturbation 190 in the vicinity of the trapping electrodes, as may be seen from Figure 3b which shows lines of equipotential in the cell 100' of Figure 3a.

Turning finally to Figure 4, a further embodiment of a cell 100" for FTMS is shown. Again, the components common to Figures 2a, 3a and 4 are labelled with like reference numerals. In the arrangement of Figure 4, each of the electrodes 110, 120, 130, 140 and 150 is selectively connectable to a.c. and d.c. voltages which are decoupled using capacitances 200. This allows for maximum flexibility. For example, each of the electrodes can first be energized with d.c. only, when the cell is first filled with ions. Thus, a trapping field can be established which has boundaries extending right to the edges of the cell 100". This trapping field can then be adjusted so as to squeeze the ions towards the centre of the cell 100"; in particular, the d.c. voltage can be adjusted on the electrodes so as to shift the potential

well towards the centre of the cell 100" until there is no more d.c. voltage on the outer excitation electrodes 140, 150 or on the central excitation electrodes 110, and the trapping field resembles that of Figure 2b. At that point, the r.f. voltage supply 160 can be applied to the excitation electrodes 110, 140, 150 to arrive at the configuration of Figure 2a, or it may be applied to all of the electrodes, excitation plus trapping, to arrive at the configuration of Figure 3a. Other static field configurations may be envisaged as a precursor to the preferred trapping/excitation arrangements.

Although some specific embodiments of the invention have been described, it will be understood that these are by way of example only and that various modifications are possible. For example, whilst in Figures 3a and 4, the r.f. and d.c. voltages are decoupled using a capacitance, an inductance may be employed instead or as well. Furthermore, although only two pairs of outer excitation electrodes have been described, additional outer excitation electrodes may be employed, so as further to reduce inhomogeneities in the excitation field in the region of the homogeneous magnetic field. Indeed, interlaced trapping/excitation/trapping/excitation arrangements may also be employed.

As a further refinement, the cell 100, 100' and 100" may be fitted with end caps (not shown) that are located at either end of the cell, adjacent the outer excitation electrode pairs 140, 150 and which are mounted coaxially with the electrodes. Preferably, these end caps have a radius somewhat less than that of the excitation and trapping electrodes so that the cell is only partially

physically closed by the end caps. This arrangement permits the field shape to be controlled still further.

As still a further alternative, the central excitation electrode pair 110 may have a different diameter and/or may not be coaxial with the adjacent trapping electrode pairs 120, 130 or the outer excitation electrodes 140, 150. This allows for compensation for the excitation field in the vicinity of the trapping electrodes, once again so as to remove or at least reduce the magnitude of the perturbation 190 (Figure 2c).

CLAIMS:

1. A measurement cell for an FTMS spectrometer, comprising:

a plurality of excitation electrodes arranged symmetrically about a longitudinal axis which extends in a direction generally parallel to the field direction of an applied homogeneous magnetic field; and

a plurality of trapping electrodes, also arranged symmetrically about the said longitudinal axis;

wherein at least some of the excitation electrodes are arranged axially outwardly of the trapping electrodes.

2. The measurement cell of claim 1, wherein the plurality of excitation electrodes comprises a central electrode set, arranged about a central point along the longitudinal axis, and first and second outer electrode sets, axially spaced from the central electrode set along that axis, and wherein the trapping electrodes comprise first and second trapping electrode sets, located axially between the outer electrode set and the first and second outer electrode sets of the excitation electrodes respectively.

3. The measurement cell of claim 1 or claim 2, further comprising an r.f. voltage supply connected to the plurality of excitation electrode, and a d.c. voltage supply connected to the plurality of trapping electrodes.

4. The measurement cell of claim 3, wherein the r.f. voltage supply is further connected to the plurality of trapping electrodes.

5. The measurement cell of claim 4, wherein the r.f. voltage supply and the d.c. voltage supply are decoupled.

6. The measurement cell of claim 5, wherein the r.f. voltage supply is capacitively and/or inductively coupled to the trapping electrodes.

7. The measurement cell of any one of the preceding claims, wherein the excitation electrodes and the trapping electrodes are each equidistantly spaced about the longitudinal axis of the measurement cell.

8. The measurement cell of any one of claims 1 to 6, wherein at least one of the excitation electrodes is radially spaced from the longitudinal axis at a first distance which is different to that of the or each of the other excitation electrodes.

9. The measurement cell of claim 2, wherein the central electrode set is radially spaced from the longitudinal axis at a first distance which is different to that of the first and second trapping electrode sets and also different to that of the first and second outer electrode sets.

10. The measurement cell of any one of the preceding claims, further comprising end caps arranged axially outwardly of the trapping and excitation electrodes.

11. The measurement cell of claim 10, wherein the end caps are located along the longitudinal axis of the cell so as partially to enclose a volume therebetween.

12. The measurement cell of any preceding claim, wherein the plurality of excitation electrodes comprises:

a first pair of curved excitation electrodes arranged symmetrically about the longitudinal axis of the cell and about a central point along that longitudinal axis;

second and third pairs of curved excitation electrodes each arranged symmetrically about the longitudinal axis of the cell, and equidistantly spaced along that axis about the central point thereof; and

first and second pairs of curved trapping electrodes, arranged symmetrically about the longitudinal axis, each trapping pair being arranged between the first pair of curved excitation electrodes and the second and third pairs of curved excitation electrodes respectively;

the cell further comprising a pair of detection electrodes radially spaced about the longitudinal axis of the cell with respect to the excitation and trapping electrodes, and having a diameter similar to the said excitation and trapping electrodes.

13. A Fourier Transform Mass Spectrometer including the measurement cell of any of claims 1-12.

14. A method of trapping and exciting ions in a measurement cell of an FTMS spectrometer, the method comprising:

(a) applying a magnetic field to the measurement cell so as to produce a region of homogeneous magnetic field, having a magnetic field direction, within the cell;

(b) applying a d.c. trapping potential to a plurality of trapping electrodes which are arranged symmetrically about a longitudinal axis which extends in a direction generally parallel to that magnetic field direction, so as to trap ions in the cell, in that axial direction; and

(c) applying an r.f. excitation potential to a plurality of excitation electrodes which are arranged symmetrically about that longitudinal axis, so as to resonantly excite the ions in the cell, at least some of the excitation electrodes being arranged axially outwardly of the trapping electrodes;

wherein the ions are trapped within the region of homogeneous magnetic field and wherein the ions are further trapped within a homogeneous region of an excitation electric field generated by the application of the r.f. excitation potential to the said excitation electrodes.

15. The method of claim 14, further comprising:

applying an r.f. excitation potential to at least one of the plurality of trapping electrodes in addition to the d.c. trapping potential applied thereto.

16. The method of claim 15, further comprising applying the r.f. excitation potential to each of the trapping electrodes along with the d.c. trapping voltage applied thereto.

17. The method of claim15 or claim 16, wherein the step of applying the r.f. excitation potential to the or each of the trapping electrodes comprises coupling the r.f. excitation potential to the or each trapping electrode via a capacitance and/or an inductance.

18. The method of claim14 or claim 15 or claim 16, further comprising, prior to at least one of the steps (a), (b) and (c):

applying a d.c. trapping potential to one or more of the excitation electrodes so as to generate a first ion trapping field; and

subsequently removing the said d.c. trapping potential from the excitation electrodes to which it has been applied.

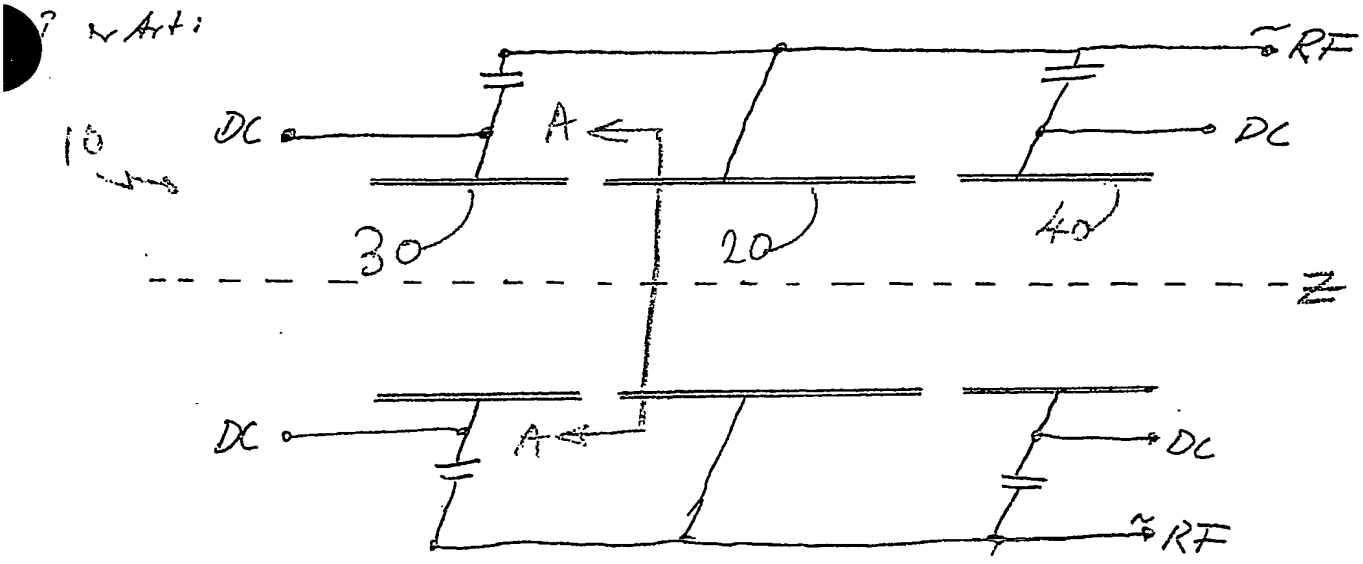


Fig. 1a

PRIOR ART

Storage Field:

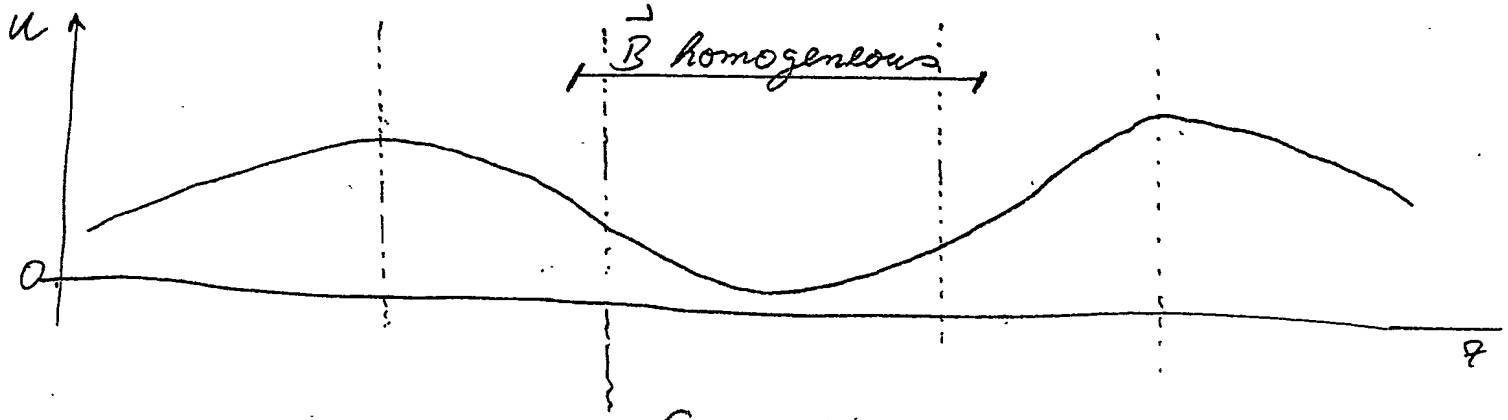


Fig. 1b

PRIOR ART

Side View:

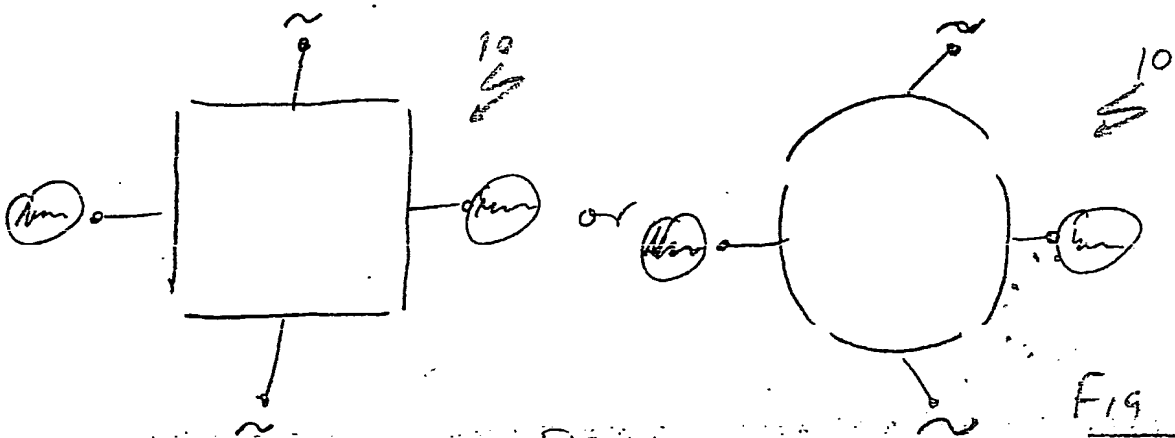


Fig 1d

Fig 1e

PRIOR ART

NOT TO BE AMENDED

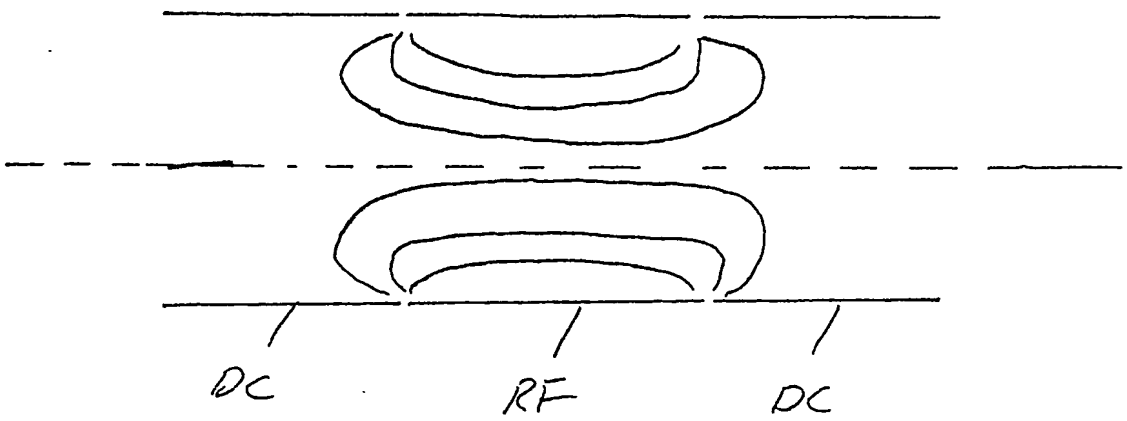


FIG 1c

PRIOR ART.

Prior Art: Excite field; isopotential lines

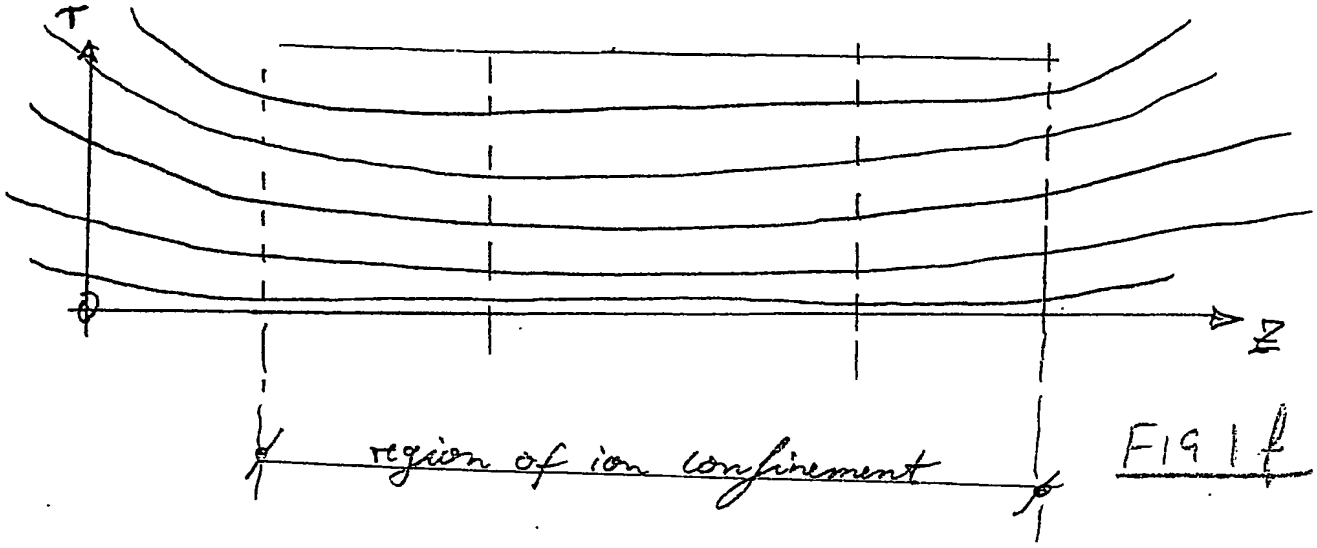


FIG 1f

Field curvature and Force $\vec{F}$; Field $\vec{E}$

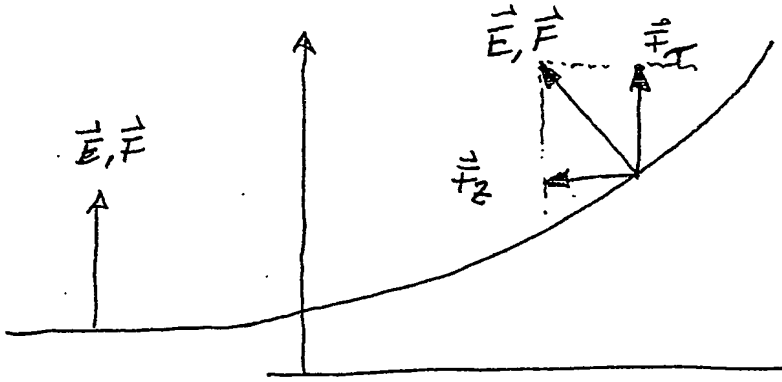


FIG. 1g.

PRIOR ART

: Segments; no excitation on trapping electrodes

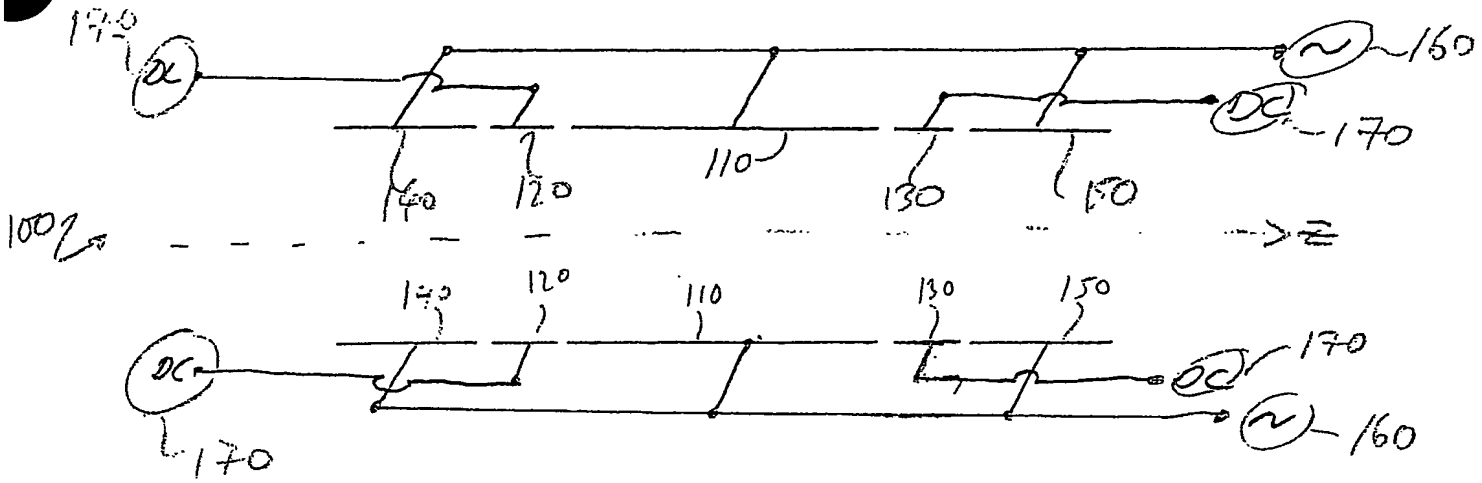


Fig. 2a

Storage field:

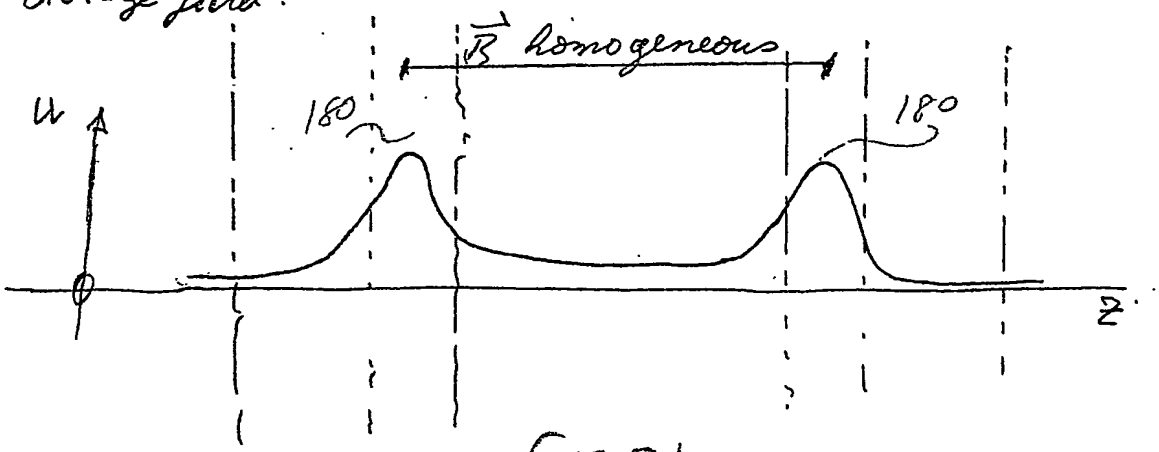


Fig. 2b

Excitation field: isopotential lines

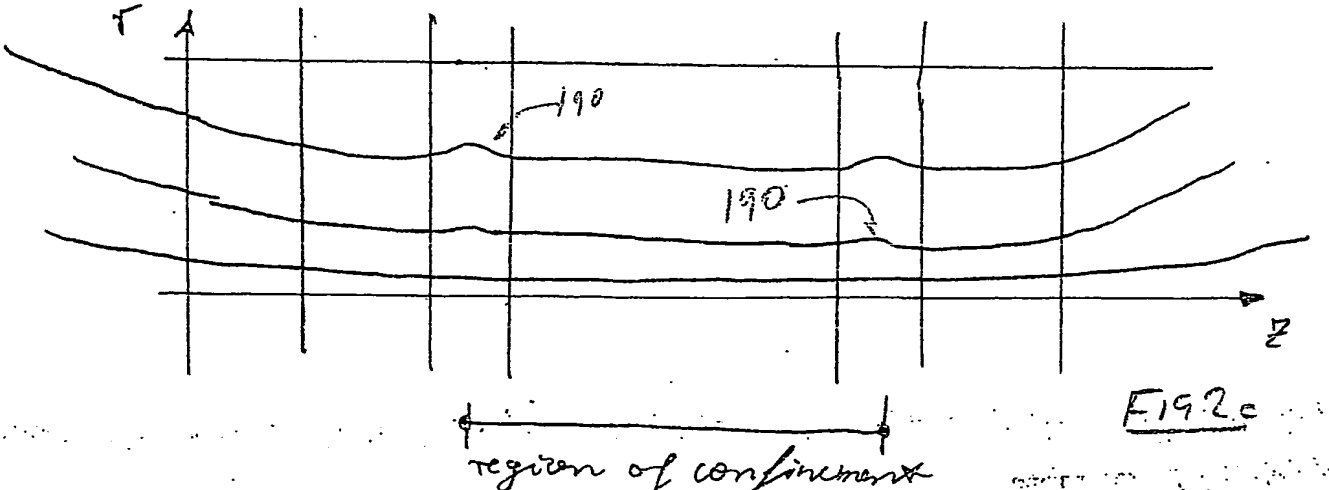
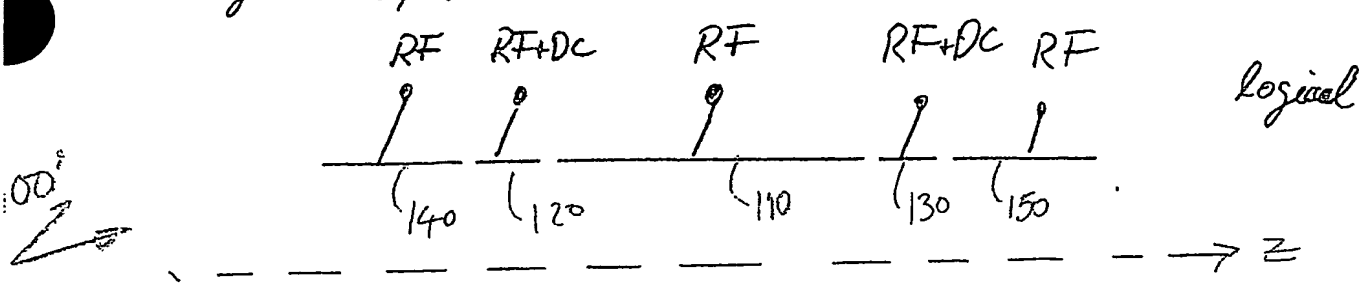


Fig 2c

Segments; excitation on all electrodes



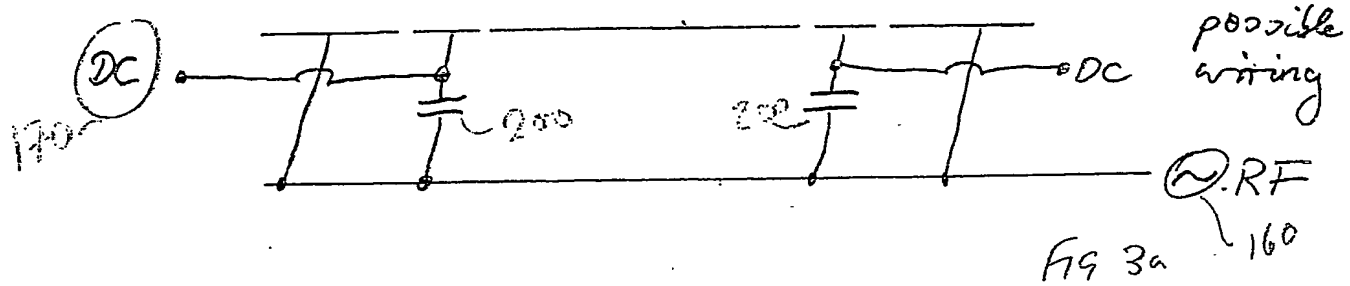


Fig 3a

Excitation field : iso potential lines

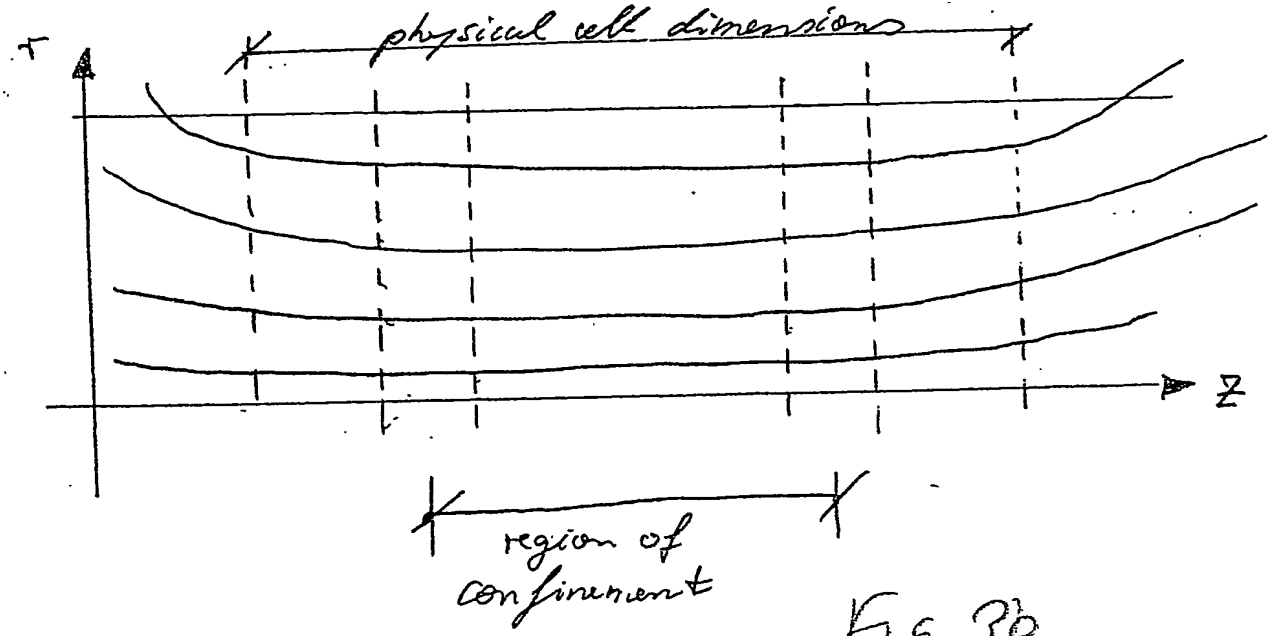


Fig 3b

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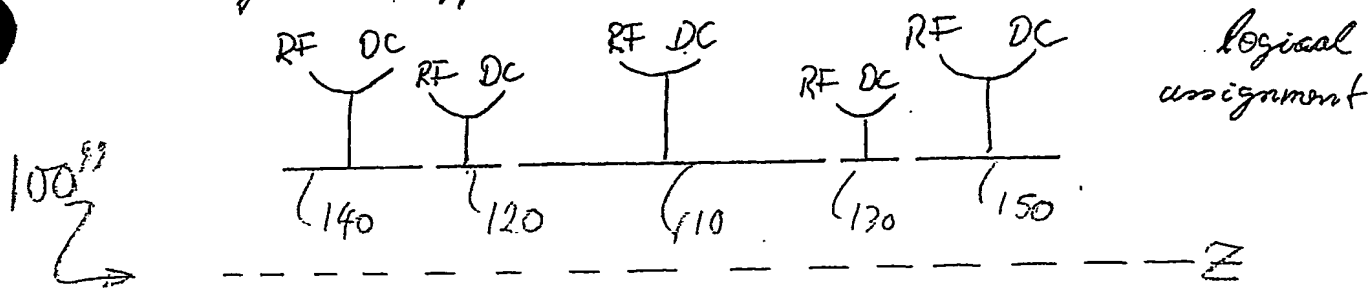
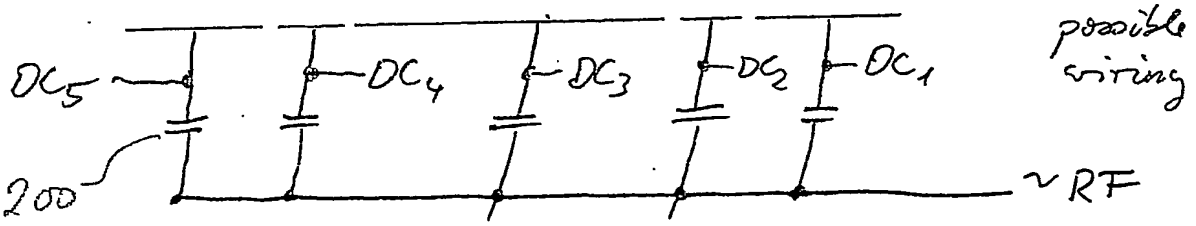
most flexible application:





allows various static field combinations, depending on use.

Fig 4

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2003